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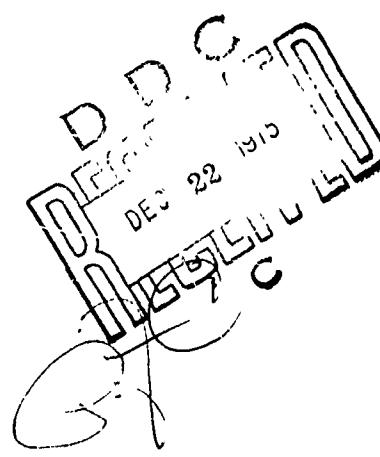
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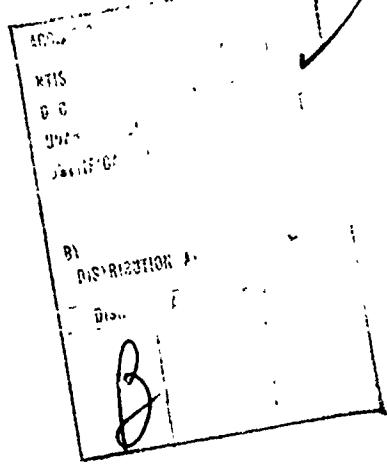
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(6) The Effects of Ultraviolet Light on
TNT in Aqueous Solutions

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THE EFFECTS OF ULTRAVIOLET LIGHT ON TNT IN AQUEOUS SOLUTION

by

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ABSTRACT

The effect of ultraviolet light on aqueous trinitrotoluene solutions has been studied in open and closed systems. Irradiation of saturated aqueous solutions of TNT in open containers for 24 hours caused a visible change in the appearance of the solutions and a drastic drop of TNT concentration from 100 ppm to 0.16 ppm. Samples pulled at intervals indicated that the TNT concentration consistently decreased with time. Photochemical conversion products of TNT were evident in samples taken after 3, 6 and 24 hours of irradiation. Aqueous solutions of 1, 3, 5 (¹⁴C) TNT were irradiated in closed vessels for periods of 24, 72, 144 and 312 hours. The activity of the irradiated TNT decreased with increased time of exposure. Labeled CO₂ was found to be one of the photolytic products indicating that ring cleavage occurred. Unidentified volatile products of the reaction were trapped by activated charcoal. Most of the photochemically converted compounds remaining in solution were found to be polar and unextractable with benzene or acetone.

FOREWARD

This study was performed by the Biological Sciences Branch of the Weapons Quality Engineering Center, NAVWPNSUPPCEN Crane. The study was originally designed to develop a pretreatment for aqueous TNT in order to render the explosive more amenable to biodegradation. However, the irradiation with ultraviolet light proved more effective than anticipated and is considered in this report as a complete treatment for aqueous TNT wastes.

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INTRODUCTION

Trinitrotoluene is a recalcitrant molecule which poses a potential pollution problem at explosive and ammunition production and demilitarization centers. A water solution of TNT, upon exposure to sunlight or artificial sources of UV light undergoes a chemical conversion into products which impart a pink or reddish coloration to the water (1, 2, 3). This fact suggests that TNT is to some measure vulnerable to the action of ultraviolet light and could be degraded by it. Studies were designed to determine the effectiveness of ultraviolet light on the decomposition of TNT under various conditions.

MATERIALS AND METHODS

Experiment 1.

A saturated aqueous solution of TNT¹ (100 ppm) was prepared by dissolving the TNT in distilled water overnight. The TNT solution was dispensed into shallow glass vessels in aliquots of 25 ml each so that the depth of the solution would be 0.5 cm. Four such samples were irradiated, uncovered, by a GE germicidal lamp (GE, 30 watt, #G30T8) at a distance of 14 cm. from the surface of the liquid to the light source. The presence of any external light was eliminated by irradiating in a windowless hood. Two 0-hour samples served as controls and duplicate samples were pulled after 1, 3 and 24 hours of exposure. These were analyzed by gas chromatography² (Beckman GC-5) to determine TNT concentration and to detect the possible presence of any conversion products which could appear during this analysis.

1 Recrystallized TNT - Naval Weapons Support Center, Crane, Indiana

2 Method QTM-GC5, WQEC Chemical Standard Test Methods, Naval Weapons Support Center, Crane, Indiana

Experiment 2.

Repeating the above procedure an aqueous TNT solution was irradiated for 24 hours at a distance of 42 cm. from the UV source. Duplicate 0-hour and 24-hour samples were taken and analyzed by gas chromatography for TNT and possible conversion products.

Experiment 3.

A 350 ml sample of a saturated water solution of TNT was prepared. Contained in an uncovered shallow glass dish at a depth of 0.5 cm., it was irradiated at a distance of 14 cm. from the UV source. Duplicate samples of the aqueous TNT solution were taken at 0, 3, 6 and 24 hours of irradiation. The samples were analyzed by gas chromatography for the presence of TNT and additional products. The pH of the solution was noted before and after photochemical treatment.

Samples of the 0-time TNT solution and the 24-hour photolysate were spotted on silica gel thin-layer chromatography plates (Quantum Industries - LQDF plates) and developed according to a standard test method for TNT and decomposition products.³

Experiment 4.

An apparatus for the irradiation of (¹⁴C) TNT solutions in a semi-closed or closed system was prepared. A Vycor glass tube (Corning Glassware 7910), 15 x 130mm, was used as the reaction vessel containing the (¹⁴C) TNT solution. The tube was fitted with a rubber stopper and connected by glass and rubber tubing to a 50 ml Erlenmeyer flask containing an alkali to trap CO₂.

³ Method QTM-TLC2, WQEC Chemical Standard Test Methods, Naval Weapons Support Center, Crane, Indiana

A 100 ppm solution of 1, 3, 5 (^{14}C) TNT was prepared and its activity determined by a scintillation counter (Nuclear - Chicago Instruments). Multisol (Isolabs, Inc.) was the scintillation cocktail used for measuring activities of labeled samples.

A 2 ml sample of the aqueous (^{14}C) TNT was introduced into the Vycor tube and this tube connected to the CO_2 trap containing 10 ml of 20% NaOH. The entire apparatus was purged with helium through a port in the stopper of the tube. After purging, all outlets were sealed but the air vent tube on the stoppered CO_2 trap remained open.

In preparation for UV treatment, the tube was angled beneath the lamp in such a manner that the average depth of the (^{14}C) TNT solution was 0.5 cm. and the distance of the lamp from the surface of the solution was 14 cm. The system was irradiated for 24 hours.

At the termination of the exposure period the system was again purged to force any $^{14}\text{CO}_2$, which may be present, into the trap. After purging, a 1 ml sample of the photolysate was measured for activity. The trapped CO_2 was converted into BaCO_3 by adding 12.5 ml of 30% NH_4Cl and 25 ml of 40% BaCl_2 to the 10 cc of NaOH from the flask. The carbonate was allowed to precipitate out upon standing. The carbonate sample was filtered through a pre-weighed scintered glass crucible and the precipitate was rinsed with acetone and dried. After drying, the crucible and precipitate were weighed and the weight of the carbonate determined so that the activity of a measured portion could be derived with the scintillation counter. The carbonate sample was added to the Multisol cocktail for calculation of activity.

The basic assay was repeated closing off the entire system. All other experimental parameters remained the same. Samples were taken at 0-time and 24 hours to measure the activity of the (¹⁴C) TNT solution and photolysate. The carbonate was precipitated from the alkali and its activity measured accordingly.

The CO₂ trap of the closed system was altered. A scintillation vial containing a disc of filter paper (the diameter of the vial) saturated with 20% NaOH was attached to the reaction vessel replacing the flask containing the NaOH solution. The irradiation process was repeated on another sample after this change, maintaining all other parameters but increasing the exposure time from 24 to 72 hours. At 72 hours the (¹⁴C) TNT solution was sampled for activity. Multisol was added directly to the vial containing the filter paper after it had been dried. ¹⁴CO₂ was thus measured from the filter paper trap in the scintillation vial.

The assay was repeated extending the irradiation time to 144 hours. Five samples were irradiated in this manner. The activity of each sample was determined before and after irradiation. One of the five had a CO₂ trap which was analyzed for activity. Thin-layer chromatography was used to assay for the presence of TNT in three of the UV treated samples and one control.

In another assay an activated charcoal trap (100 mg) was inserted between the reaction vessel and the CO₂ trap. Maintaining all other parameters, the (¹⁴C) TNT solution was irradiated for 312 hours and the activity of the labeled solution was determined before and after irradiation. The charcoal trap was completely oxidized by a carbon analyzer (Leco Carbon Determinator) to convert it to CO₂ for measurement of

activity. As the charcoal was oxidized to CO_2 it was trapped in a solution of 20% NaOH which was treated accordingly to precipitate any $\text{Ba}^{14}\text{CO}_3$. The activity of a sample of this carbonate was determined. Multisol was added to the vial containing the filter paper CO_2 trap and the activity of any $^{14}\text{CO}_2$ produced by the system itself was measured.

RESULTS AND DISCUSSION

Experiment 1.

After 24 hours of UV irradiation in an open system aqueous saturated solutions of TNT lose their identity physically and chemically. Clear, colorless solutions of 100 ppm TNT were transformed into turbid rusty-colored solutions after such exposure. Table 1 illustrates the effects of time and the photochemical action of UV light on TNT as determined by gas chromatography.

TABLE 1. UV Exposure Time of TNT Solution vs TNT Concentration

TIME (HR.)	PPM TNT
0	98, 100
1	101, 97
3	92, 88
24	≤ 1 , ≤ 1

After being irradiated for 24 hours TNT had apparently undergone some photochemical decomposition which resulted in its physical and chemical transformation. Duplicate samples confirmed this change as is indicated by a decrease in TNT concentration with time. The time of exposure under these conditions appears to be a critical element since there was a drastic change in TNT concentration from 100 ppm at 0-time to ≤ 1 ppm after 24 hours.

Experiment 2.

The effect of ultraviolet irradiation on aqueous solutions of TNT under given conditions is influenced by the distance of the sample from the light source. A sample irradiated at distance of 42 cm. from the UV source yielded no change in TNT concentration over a 24-hour irradiation period. A sample irradiated from a distance of 14 cm. for the same length of time yielded over a hundred-fold decrease in TNT in the open system.

Experiment 3.

The irradiation of large volumes of aqueous TNT (100 ppm) appeared to yield results comparable with those of Experiment 1. (See Table 2.) Analysis by gas chromatography also indicated the presence of additional components (TNT conversion products) in solution. These were illustrated by additional peaks accompanying the TNT peak during the analysis for TNT.

TABLE 2. Exposure Time vs TNT Concentration. Note the Presence of Additional Components

TIME (HR.)	PPM TNT	NO. ADDITIONAL COMPONENTS
0	106, 105	0
3	65, 68	5, 4
6	26, 27	5, 5
24	0.17, 0.16	4, 4

Of these components only one could be identified. This was found to be 4 amino-2,6 dinitrotoluene. All other conversion products remained unidentified and were unlike any compounds normally found as products of the microbial degradation of TNT (unpublished data).

As can be seen from Table 2, TNT concentration decreased with increased exposure time. As the concentration decreased additional components appeared. The only product, however, consistently present at all intervals of sampling was 4 amino-2,6 dinitrotoluene. There was no pattern as to the appearance or disappearance of the other conversion products with time.

The pH of the 0-time sample was found to be 6.6. After 24 hours of irradiation it was 3.65. It is obvious that TNT is indeed undergoing some type of major photochemical alteration contributing to the drastic change in pH. Samples were not taken at intermediate intervals for pH determinations so it was not possible to determine if the change was sudden or if it fluctuated with time or if the pH decreased as the TNT concentration decreased.

Analysis by thin-layer chromatography indicated that at 0-time only TNT was present. After 24 hours of irradiation four conversion products and a trace (0.25 ppm) of TNT were evidenced. One of these components was identified as 4 amino-2,6 dinitrotoluene. This supports the data found by gas chromatography.

The previous assays give a good indication that under given conditions time has a direct bearing on the disappearance rate of TNT by ultra-violet light. The distance of the sample from the light source also appeared to influence the effectiveness of UV light in degrading TNT in such a system. The results further indicated that TNT is converted into several components as a result of photochemical changes induced by this irradiation.

In all of these experiments it must be emphasized that sample irradiation was performed in open systems. Aqueous solutions of TNT

were subjected to evaporation and concentration upon exposure for any extended length of time. Since ultraviolet light could have induced the formation of ozone, it was difficult to determine if the irradiation alone or if the combination of UV light and O_3 contributed to the decomposition of the TNT solutions. It was important, therefore, to create a system which would, for the major part, exclude or reduce the effects of ozone on the system and eliminate evaporation and concentration.

Experiment 4.

Irradiation of samples of (^{14}C) TNT in a semi-closed or completely closed system eliminated the influence of the aforementioned factors to a great extent and yielded results which indicated that TNT concentration and the presence of conversion products were influenced by exposure time to UV light.

The results in Table 3 show that the percent activity found in the irradiated (^{14}C) TNT solution decreased with increasing exposure time to UV light. It is also interesting to note that the physical appearance of the (^{14}C) TNT solution changed with increased exposure to UV light as it had done in experiments using an open system. At 0-time the sample was clear and colorless. At 24 hours it had turned yellow but at 72 hours it was clear and colorless again.

TABLE 3. The percentage of total, initial activity recovered in various fractions resulting from irradiation of (^{14}C) TNT solutions with UV light.

TYPE SYSTEM	HR.	%ACTIVITY IN SOLUTION OF (^{14}C) TNT	%ACTIVITY TRAPPED ON CHARCOAL	%ACTIVITY AS $^{14}\text{CO}_2$	UNRECOVERED ACTIVITY
AFTER IRRADIATION					
Semi-closed	24	68	-	10	22
Closed	24	68	-	9	23
Closed	72	23	-	15	62
Closed	144	36*	-	17*	47*

*Different type Vycor test tube used as reaction vessel; #7900 glass not as penetrable by UV light as #7910 used in the major part of the experimentation.

A portion of the activity was found to be in the form of $^{14}\text{CO}_2$. This indicates that ring cleavage of the TNT molecule must have occurred since the labeled portion of the ring included only the 1, 3 and 5 positions. However, as can be seen in Table 3 a fraction of the activity was not recovered.

To determine the consistency of the results with a definite exposure period, four samples of (^{14}C) TNT water were prepared and irradiated for 144 hours in a closed system, but $^{14}\text{CO}_2$ activity was not measured in all samples. Table 4 shows the consistency of the recovered activity of the solutions as ranging from 12-17%.

With increasing exposure time a large portion of the activity was not recovered (Table 3). In an effort to capture the labeled organic products of photolysis which were being lost, an activated charcoal trap was inserted in the system. The use of such a trap resulted in the recovery of approximately 55% of the expected total activity, as can be seen in Table 4. However, approximately one quarter of the activity still escaped detection. This, perhaps, could be attributable to a failure in trapping 100% of the activity on the charcoal during its complete oxidation.

Analysis by thin-layer chromatography of samples a, b, c (Table 4) irradiated for 144 hours indicated that TNT was present in samples b and c in concentrations of ≤ 0.025 ppm. The same conversion product appeared in a and c at a concentration barely discernible by TLC work. This component was not identified. TLC analysis of the 312 hour sample resulted in no detection of TNT or conversion products.

TABLE 4.

TYPE SYSTEM	HR.	%ACTIVITY IN SOLUTION OF (^{14}C) TNT	%ACTIVITY TRAPPED ON CHARCOAL	%ACTIVITY AS $^{14}\text{CO}_2$	UNRECOVERED ACTIVITY
AFTER IRRADIATION					
Closed	144	13	-	-	87
Closed	144	17 ^a	-	-	83
Closed	144	12 ^b	-	-	88
Closed	144	20 ^{c*}	-	-	80*
Closed -					
Charcoal trap	312	5	55	17	23

*Different type Vycor test tube used as reaction vessel; #7900 glass not as penetrable by UV light as #7910 used in the major part of the experimentation.

It is very interesting to note that approximately 30% of the activity remaining in the photolysate after 144 hours of irradiation was detected in the water fraction after extraction with benzene and acetone. This indicates that some of the decomposition products are polar. These products, also, have yet to be identified.

The data accumulated from closed system experimentation attests to the fact that ultraviolet light could be very instrumental in degrading TNT. UV light had effected a tremendous decrease in TNT concentration in aqueous solutions in open systems and had eliminated TNT and decomposition products completely in closed system. Future experimentation could decide its total effectiveness on larger systems alone or in combination with biologically active systems.

Previous studies have indicated that microorganisms do degrade TNT by converting TNT into various products (4,5). The original basis of our studies was to attempt to make TNT more amenable to biodegradation by microorganisms. Feeling that this could be achieved photochemically, saturated solutions of TNT were irradiated and the photolysates used in the preparation of enrichment media for selection of microbial flora capable of attacking these photochemical conversion products. In this process we determined that ultraviolet light itself was an excellent tool in degrading TNT. This degradation due to UV light absorption was dependent on several parameters including exposure time, distance from source, and the type system employed. Further experimentation with these and other factors may determine the effectiveness of UV light alone or in combination with microorganisms in the elimination of TNT as a harmful pollutant.

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